

## D. COLLOID-FACILITATED RADIO-NUCLIDE TRANSPORT

The role of colloids in the transport of contaminants through the subsurface was reviewed by McCarthy and Zachara (1989). These authors concluded that the existing data suggest that colloidal species can enhance contaminant transport in the subsurface in the vadose and the saturated zones. McCarthy and Zachara also pointed out that the existing information is inadequate to assess the importance of colloid-facilitated transport or to develop a capability to predict contaminant migration that includes colloids. The work of McCarthy and Zachara identified several research needs: development of sampling techniques and predictive capabilities to determine the occurrence and properties of subsurface colloids, experiments and predictive transport models to assess the mobility of subsurface colloids, and data on the sorption of contaminants onto colloids to evaluate the implications of colloids for contaminant transport in the subsurface.

Ramsay (1988) reviewed the role of colloids in the release of radionuclides from a nuclear waste repository. He defines colloids as particles in the size range from 1 nm to 1 mm with large surface areas (on the order of 1000 m<sup>2</sup>/g for the smallest particles). He points out that the role of colloids in migration involves many processes, such as enhancement of the source term by the leaching of the radionuclides in colloidal form from the waste form, degradation of the waste form (by bacterial action) to produce fine particulates, and sorption of radionuclides onto colloids present in the groundwater. Ramsay also points out that although it is clear that colloids exist, their significance in affecting radionuclide migration is not clear.

Ramsay's work describes three general cases for colloid-facilitated radionuclide migration based on colloidal charge. First, uncharged colloids (whose particle sizes are considerably smaller than the pore or fracture size of the medium) migrate without retardation. Second, charged colloids with the same sign as the surface charge of the medium are

repelled by the medium walls, and there is a net increase in the flow velocity of the colloids. Third, the colloids and the medium surfaces have opposite charges, which can result in a slowing down of the colloids by their interaction with the medium.

There are two main categories of colloids in the subsurface in a nuclear waste repository: groundwater colloids and anthropogenic colloids. Groundwater colloids (Kim 1991) occur naturally in aquatic systems and consist of inorganic or organic molecular constituents or microorganisms. Anthropogenic colloids are colloids produced by physical, chemical, or biological processes acting on human-introduced materials. These include radioactive waste-derived colloids and colloids derived from other materials and activities related to waste isolation.

Radioactive waste-derived colloids include:

- degradation colloids generated directly from the waste form by disaggregation or spalling of actinide solid phases;
- precipitation colloids generated from solutions supersaturated with respect to actinide solid phases, including real actinide colloids produced by the agglomeration of hydrolyzed actinide ions, traditionally referred to as radio-colloids; and
- pseudocolloids generated by the attachment of radionuclides (in soluble or colloidal form) to other colloids (such as groundwater colloids).

The objectives of this section are to describe colloid transport models that can be used to assess the importance of colloid-facilitated radionuclide migration, summarize the observations of the existence of colloids from sampling studies and the evidence of colloid transport at the field scale, list the potential sources of colloids at Yucca Mountain, review the colloid transport experiments relevant to a potential nuclear waste repository at Yucca Mountain, and summarize the research questions that need to be answered to predict the role of

colloids in the release of radionuclides from a potential repository at Yucca Mountain.

## Colloid Transport Calculations

The major processes that may occur during the migration of colloids in the subsurface are colloidal generation, sorption of radionuclides onto colloids in the groundwater, attachment/detachment of colloids, agglomeration of colloids in the groundwater, and exclusion of colloidal particles from pores due to size or surface-charge considerations. The limited applicability of filtration theory to describe particle transport through porous media has been discussed by McDowell-Boyer et al. (1986) who concluded that data were needed on particle retention, aggregate formation, permeability reduction, and the potential for erosion by changes in flow or solution chemistry before colloid transport through a natural aquifer could be predicted. Smith and Degueldre (1993) pointed out the limited applicability of filtration theory to describe colloid transport through fractured media in which colloid-wall interactions are important. Kessler and Hunt (1993) described the result of deposition and erosion of colloids in fractured media. They reported that colloids suspended in the water in fractures will deposit on fracture surfaces and partially or completely clog the fracture; the degree of clogging depends on whether deposited colloids can erode from the surfaces of the fractures. When the fracture remains only partially clogged, the unclogged portion becomes an open channel. Kessler and Hunt predict that for repository conditions (involving very low flow rates of  $\sim 1$  m/yr), erosion will not occur and the colloids will not travel very far because the fractures are expected to clog up completely with colloids.

The transport code CTCN (Colloid Transport Code–Nuclear) was developed within the Yucca Mountain Site Characterization Project for the study of colloid transport in porous and fractured media under unsaturated and saturated conditions (Jain 1991). The code was designed to solve both the unsteady-population-balance equations and the

mass, energy, and momentum equations in up to four axes using the Method of Lines with Modified Gear Method to solve the population-balance equation. It is written in FORTRAN 77 and is capable of running on SUN, VAX, and CRAY systems. CTCN maintains a mass balance of the particles in the system and is capable of taking into account the likely colloid transport phenomena to describe migration of colloids through a natural medium. Most other colloid transport calculations (for example, Smith and Degueldre 1993) are performed with transport codes for soluble contaminant migration using parameters and boundary conditions that simulate the behavior of colloids.

Colloid-facilitated radionuclide transport was investigated in two dimensions for saturated and unsaturated fractures by Nuttall et al. (1991) using CTCN. A steady-state parabolic-flow-velocity profile was assumed for these calculations and a step input of colloids was used as a boundary condition to introduce particles into the fracture. The dynamic two-dimensional population-balance equation was solved numerically using CTCN. In the study by Nuttall et al., only the effects of capture and release mechanisms of the colloid transport model were studied. Agglomeration of colloids, pore size exclusion, particle growth, and size distributions were not taken into account in this work. The results of Nuttall et al. indicate that the diffusion rate of colloids in the direction perpendicular to the flow is an important parameter and the rate-controlling step for colloids diffusing to the fracture wall and being captured. The diffusion rate of colloids is approximately three orders of magnitude smaller than the diffusion rate for molecular species; consequently, colloids can transport long distances in fractures even with irreversible capture at the rock-water interface. Smaller particles are more likely to come in contact with the rock-water interface, but physical capture depends upon the electrokinetic and van der Waals forces. Nuttall et al. also report that for unsaturated conditions, hydrophobic colloids will preferentially collect at the air-water interface and transport at the highest water velocity.

Smith (1992) explored the influence of nonlinear sorption on colloid-facilitated radionuclide transport through fractured media. Smith and Degueldre (1993) also explored the result of different solute-colloid sorption mechanisms on radionuclide transport. Smith and Degueldre concluded that the assumption of fast, linear, and reversible radionuclide sorption onto colloids is nonconservative in the prediction of colloid-facilitated radionuclide transport. Smith and Degueldre's work suggests that the time for desorption (days or weeks) exceeds the time for sorption (seconds or minutes) in the radionuclide-colloid interactions. Consequently, it is important to determine the degree of completeness of desorption; irreversible sorption of the radionuclide onto the colloid may be present. If colloids migrate over long distances and are excluded from wall-rock pores due to their size, irreversible sorption would increase the rate of radionuclide transport in the subsurface. Smith and Degueldre concluded that for cases involving irreversible radionuclide-colloid sorption, the transport of radionuclides is strongly dependent on the extent of colloid interaction with the fractures.

## **Evidence of Colloids and Colloid Transport from Field Studies**

### **Natural analog sites**

#### *Cigar Lake uranium deposit.*

The colloids (< 1 mm) and particulate matter (> 1 mm) at the Cigar Lake uranium ore deposit in Canada were characterized by Vilks et al. (1988). The deposit is located at a depth of 400 m and has not been disturbed by mining operations or surface weathering. The ore is surrounded by a clay-rich zone containing iron hydroxides. The clay zone is surrounded by an altered sandstone separated from the surrounding unaltered sandstone by a silica-rich cap in which quartz has filled most of the fractures. Vilks et al. report that 1) the total particle concentration in groundwater at Cigar Lake ranges from 0.6 to 261 mg/l; 2) groundwater particles consist of clay minerals, iron-silicon precipitates, organics, rock particles, and drilling products; 3) the natural colloids and suspended particles in the

groundwater at Cigar Lake contain significant amounts of uranium, thorium, and radium-226; 4) uranium dispersion has not been significant beyond the quartz cap; 5) there is no evidence of uranium migration away from the deposit; 6) radioactive colloid concentrations are low in the overlying sandstone and in the groundwater down-gradient from the deposit; and 7) no significant migration of colloids and suspended particles away from the uranium ore deposit to the surrounding sandstone has occurred.

#### *Koongarra uranium deposit.*

Groundwater and particles from boreholes at the Koongarra uranium deposit in Northern Australia were characterized by Payne et al. (1992). The chemistry at Koongarra groundwaters is dominated by magnesium and bicarbonate, the pH is between 6 and 7.5, and the Eh ranges from 100 to 300 mV. The colloids (< 1 mm) and the particles (> 1 mm) in the Koongarra groundwaters include clay minerals and fine quartz grains. Iron was observed by Payne et al. as particle coating and as a separate colloidal form. They also report that 1) uranium migrates at Koongarra mostly as dissolved species; 2) thorium and actinium are mostly associated with immobile particles (> 1 mm); 3) of the small fraction of thorium that passes through a 1-mm filter, a large fraction is associated with colloids; 4) actinium appears to be more mobile than thorium and is associated with colloids to a greater extent, although in small concentrations; and 5) it is possible for trivalent and tetravalent actinides to migrate as colloids away from a nuclear waste repository.

#### *Pocos de Caldas Plateau sites.*

The characterization of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro de Ferro analog sites at Pocos de Caldas, Brazil, was reported by Miekeley et al. (1991). These sites are located in the center of the Pocos de Caldas Plateau. Uranium is mined by open-cast methods at Osamu Utsumi. Morro de Ferro is a thorium and rare-earth-element ore body that is 14 km from the Osamu Utsumi mine. The Morro de Ferro hill is 140 m above local stream

level and is in an advanced state of weathering.

The groundwaters at the Osamu Utsumi uranium mine are of the potassium-iron-sulfate type, oxidizing (values of Eh from 200 to 400 mV), and slightly acidic (values of pH from 5.4 to 6.1), the result of weathering of highly leached potassium-rich rocks. An upward groundwater flow gradient at the mine forces reducing water to ascend into more oxidizing environments. This process is responsible for the formation of ferric oxyhydrates in the suspended particles ( $> 0.45 \text{ mm}$ ) and in the colloids ( $1.5 \text{ nm}$  to  $0.45 \text{ mm}$ ) in the groundwaters.

The Morro de Ferro ore body is in a much more advanced state of weathering than the mine. The ore body has very high concentrations of thorium and rare-earth elements in the soil and weathered rocks and much lower concentration of uranium. Groundwater was sampled at several points down-gradient from the ore body at Morro de Ferro. The gradient extends from strongly oxidizing (Eh from 450 to 650 mV) to a less oxidizing, unperturbed environment (Eh from 200 to 450 mV).

Concentrations of dissolved organic carbon in the groundwaters from the mine and the ore body range from 1 to 4 mg/l. In shallow waters (in the unsaturated zone) at the Morro de Ferro ore body, concentrations of 10 to 20 ppm of dissolved organic carbon were occasionally observed.

Miekeley et al. (1991) report that 1) a colloid concentration at the uranium mine and the ore body of less than 1 mg/l (consisting of Fe(III) oxyhydroxides and humic-like particles in the size range from  $1.5 \text{ nm}$  to  $0.45 \text{ mm}$ ); 2) small amounts of uranium and other elements, but significant amounts of thorium and rare-earth elements concentrated in the colloidal phases and suspended particles; 3) high concentrations of colloidal humic-like materials in surface and near-surface waters, which is the reason for the much higher concentrations and proportions of thorium and rare-earth elements in colloidal fractions of organic-rich waters of the Morro de Ferro; 4) solution and colloidal phases in equilibrium

with respect to  $^{234}\text{U}$  to  $^{238}\text{U}$  isotopic ratios and identical rare-earth-element distribution patterns for these phases; 5) unfiltered groundwaters with low to moderate concentrations of suspended particles ( $> 0.45 \text{ mm}$ ), that is, 0.2 to 0.4 mg/l for the mine and 1 to 5 mg/l for the ore body; and 6) no evidence of significant subsurface transport of suspended particles or colloids in either the Osamu Utsumi mine or the Morro de Ferro ore body.

## Test sites and other areas

### *Gorleben area.*

Colloids in groundwaters from the Gorleben area, the site for the future German repository, were characterized by Dearlove et al. (1991). The geohydrologic system at Gorleben comprises glacial sand-silt aquifers associated with a Zechstein salt diapir. Dearlove et al. report that 1) the colloid concentration in the Gorleben groundwaters is  $10^{17}$  particles/l; 2) the bulk of the actinide and lanthanide elements in these groundwaters is associated with humic colloids; 3) the  $^{234}\text{U}$  to  $^{238}\text{U}$  ratio indicates that uranium in the colloidal fraction is not in equilibrium with the uranium in solution; 4) the colloids in the Gorleben aquifer are in the size range from  $1.5$  to  $15 \text{ nm}$ ; and 5) the dissolved organic carbon in these groundwaters is composed of humic and fulvic acids. Kim (1991) reports that regardless of different redox fronts, plutonium and americium are always associated with colloids in the Gorleben groundwaters and that plutonium and americium pseudocolloids play an important role in the migration or retention of radionuclides in the subsurface.

### *Grimsel Test Site.*

The characterization of colloids flowing in a fracture in the Grimsel Test Site was carried out by Degueldre et al. (1989a). The Grimsel Test Site is considered an example of a granitic-granodioritic far-field environment. The site is located in granite in the Swiss Alps about 1750 m above sea level and 450 m below land surface. A concentration of colloids of  $10^{10}$  particles/l in the size range from  $0.04$  to  $1 \text{ mm}$  was found in the Grimsel Test Site groundwater. The particles are a mixture of silica

and organic material.

## *Whiteshell Research Area.*

The Whiteshell Research Area is located in southern Manitoba, Canada, and is an example of fractured granite. Vilks et al. (1991) report that the upper 500 m of the geohydrologic systems at this site are connected by three major subhorizontal fracture zones partially interconnected at the surface by near-vertical fractures. At depths greater than 350 m, waters have a salinity between 1 and 15 g/l, a pH of 6.1 to 7.7, and are dominated by sodium, calcium, chloride, and sulfate. At shallow depths (50 to 350 m), the salinities of the waters range from 0.3 to 1.0 g/l, the pH ranges from 7.4 to 8.9, and the waters contain mainly sodium, bicarbonate, and to a lesser extent calcium. Both the shallow and deep waters are close to saturation with respect to calcite. Vilks et al. report that the average colloid concentration (in the size range from 10 nm to 0.45 mm) is  $0.34 \pm 0.34$  mg/l and the suspended particle concentration is  $1.3 \pm 3.0$  mg/l. Particles consist of aluminosilicates, carbonates and iron oxides. Vilks et al. conclude that naturally occurring colloids (in the size range from 10 nm to 0.45 mm) will have a minimal effect on radionuclide transport, provided radionuclide sorption onto colloids is reversible. They point out that if radionuclide sorption onto colloids is irreversible, colloid-facilitated radionuclide transport may be important. If so, then information describing colloid concentrations, colloid stability, and the migration properties of colloids in granite fractures will become necessary.

## *El Berrocal site.*

The El Berrocal experimental site is located 92 km southwest of Madrid (Gomez et al. 1992) in a fractured and weathered granitic formation. Uranium-bearing quartz dike/breccia intersects the excavated Berrocal site. Preliminary results indicate 1) the presence of particles in groundwaters at El Berrocal in the size range from 50 nm to 1 mm; 2) particles mainly consisting of silica, aluminosilicates, oxyhydroxides, and organic material; 3) dilute groundwaters that are slightly oxidizing to oxidizing

(Eh of 4 to 379 mV); and 4) sulfide colloidal phases in the slightly oxidizing groundwaters.

## *Shallow aquifer in a semiarid region at Los Alamos.*

Treated liquid wastes containing traces of plutonium and americium are released into Mortandad Canyon within Los Alamos National Laboratory boundaries (Penrose et al. 1990). The shallow alluvium of Mortandad Canyon is composed of sandy to silty clays formed by weathering of volcanic rocks. Penrose et al. observed detectable amounts of plutonium and americium in monitoring wells as far as 3390 m down-gradient from the discharge even though Laboratory sorption studies predict that the movement of plutonium and americium will be limited to less than a few meters. Penrose et al. report that there is very strong evidence that plutonium and americium are associated with colloidal materials (in the size range from 25 nm to 0.45 mm) in a way that is effectively irreversible and that colloidal materials can be mobile for great distances.

## *Nevada Test Site and environs.*

Kingston and Whitbeck (1991) characterized the colloids found in twenty-four springs and wells in central and southern Nevada in a region underlain by carbonate rocks. The majority of the sites are on or within 50 km of the Nevada Test Site; other sites are located near Hiko and Tonopah, Nevada.

Kingston and Whitbeck report particle concentrations in the following size ranges: 0.03 to 0.1 mm, 0.1 to 0.4 mm, 0.4 to 1 mm, and greater than 1 mm. They defined colloids as stable particles in suspension in the size range from 1 nm to 1 mm and then concluded the following: 1) Most of the groundwaters studied have colloid concentrations in the range from 0.28 to 1.35 mg/l; three sites have high colloid concentrations that range from 6.48 to over 25 mg/l. 2) Colloid concentrations are similar regardless of hydrologic setting, aquifer lithology, or geographic location. 3) No obvious correlation exists between water chemistry and colloid concentrations in the waters studied. 4) Silica



(but not quartz) is present in all the colloids collected; relatively small amounts of clay or zeolite are found in all samples; calcite appeared in some samples but may be an artifact of the procedures used; and the organic structures identified in the colloidal fractions are indicative of humic- or fulvic-acid coatings on the mineral colloid surfaces. 5) Their ubiquitous presence indicates that colloids travel successfully through the subsurface at the Nevada Test Site; similar concentration distributions of sizes may indicate that groundwater flow at the Nevada Test Site is controlled by faults and fractures. 6) Silica colloids can sorb cesium, cobalt, and europium; comparison of sorption distribution coefficients for colloids and tuff suggests that europium may preferentially sorb to the colloids rather than to the tuffaceous rocks of the Nevada Test Site.

Minai et al. (1992) isolated humic material from water from Well J-13; the carboxylate group concentration reported was 2.7 meq/g for the fulvic acid fraction and 4.6 meq/g for the humic acid fraction. Minai et al. report that their procedures to isolate the organic fraction were only able to recover 1 to 5 per cent of the total organic component in J-13 water; they based this information on work by other authors that report the total organic content in J-13 water to range from 0.15 to 0.54 ppm.

Field studies of radionuclide migration from underground nuclear tests at the Nevada Test Site have been carried out since 1974. Buddemeier and Hunt (1988) reported the transport of colloidal contaminants in groundwater away from the cavity of the Cheshire event, fired on February 14, 1976, with a yield in the 200 to 500 kiloton range. The Cheshire site is on Pahute Mesa. The nuclear test was performed at a depth of 1167 m in a formation consisting of fractured rhyolitic lavas. The pre-shot water level was at a depth of 630 m. Buddemeier and Hunt (1988) conducted filtration and ultrafiltration studies on groundwater samples from the seven-year old cavity of the Cheshire event and from the fractured lava and tuff formation 300 m down-gradient from the cavity. Substantial con-

centrations of submicrometer colloids and significant radionuclide concentrations were found at both locations. A significant fraction of the radioactivity at both locations was associated with colloidal particles ranging in size down to 3 nm; lanthanide and transition-metal radionuclides were completely associated with particulates.

Buddemeier and Hunt (1988) concluded that 1) a strong association exists between colloids and radionuclides and 2) both the dissolved and colloidal radionuclide species migrate through the interconnected fractures.

## **Detailed Colloid Analyses of J-13 Water at the Nevada Test Site**

As pointed out earlier, Harrar et al. (1990) concluded that there is considerable justification for the use of Well J-13 water as a baseline, or reference, water for the Yucca Mountain Project investigations. Part of the justification is their conclusion that a major portion of the water produced by Well J-13 originates in the Topopah Spring Member of Paintbrush Tuff, the same stratigraphic unit as the one proposed for the repository. We used water from Well J-13 at the Nevada Test Site for particulate analysis. Comparison of the water chemistry data for Wells J-13 and UE-25 p#1 (Table 3 and Figs. 6 and 7 in Chp. I: Introduction) indicates that determination of colloid concentration in water from Well J-13 would likely provide conservative estimates of the colloid concentration in Yucca Mountain groundwaters, given that colloid stability decreases with increasing groundwater ionic strength.

Water from Well J-13 has previously been used for particulate analysis, and the results have been reported by Ogard (1987). He diverted water from Well J-13 into a mobile laboratory at a rate of ~1 l/min and used a prefilter to remove particles larger than 10  $\mu\text{m}$ . He then filtered the water through a large stainless-steel filter assembly (One-Sevener Nucleopore Filter Assembly) loaded with seven 0.4- $\mu\text{m}$  membrane filters mounted in parallel. Approximately half of the water filtered through this

assembly subsequently passed through another filter system (Amicon Hollow Fiber Filter) that removed particulates with diameters greater than  $\sim 5$  nm. Thus, the particle size of the material caught by the  $0.4\text{-}\mu\text{m}$  filter system should range from  $0.4$  to  $10\text{ }\mu\text{m}$ , or  $400$  to  $10,000$  nm (large-size fraction), and the particle size of the material caught by the  $5\text{-nm}$  filter system should range from  $0.005$  to  $0.4\text{ }\mu\text{m}$ , or  $5$  to  $400$  nm (small-size fraction).

A filtration run conducted for 14 days yielded a sediment concentration for the large-size fraction of  $\sim 2.7 \times 10^{-5}$  g/l, and a sediment concentration that was only 1 per cent of this value for the small-size fraction. The large-size particulate fraction was removed from the filter system with ultrasonic treatment, dissolved in acid, and analyzed for cation composition by emission spectroscopy. The weight percentages were silicon 60%, iron 20%, calcium 11%, and aluminum 4%. A similar analysis of the small-size particulate fraction, collected from the hollow-fiber system by backflushing with Nanopure water, yielded sodium 44%, silicon 42%, calcium 8%, and iron 4%. The iron-rich particulates are suspected to be the result of contamination from the steel piping and pumping systems used in the well.

Ogard (1987) assessed the importance of particulates in the transport of radionuclides at Yucca Mountain, basing his assessment on the particulate concentration in J-13 water that he reported ( $\sim 2.7 \times 10^{-5}$  g/l for particles in the range from  $0.4$  to  $10\text{ }\mu\text{m}$ ) and reversible sorption of radionuclides onto colloidal species. Ogard concluded that the particulates in the J-13 well water would have to exhibit a sorption distribution coefficient greater than  $4 \times 10^6$  ml/g for a given radionuclide for pseudocolloids to contribute more than 10 per cent to the total amount of radionuclide migrating through Yucca Mountain. Ogard points out that sorption distribution coefficients of that magnitude have not been observed for the sorption of any radionuclide in the high-level waste onto tuff.

## Particle size distribution in J-13 water

More recently, Los Alamos National Laboratory staff collected samples from Well J-13 to assess the particle size distribution in this water. The apparatus used for this effort (Fig. 124) incorporates serial filters of three different sizes to filter the water. Before and after each filtration (sample points A through D), water samples were obtained that ranged from unfiltered to highly filtered water ( $< 5$  nm). The samples were collected in two different types of containers: borosilicate glass and Teflon™ and some were diluted with Nanopure water immediately after collection at a volume ratio of Nanopure water to J-13 well water of 3 to 1.

Collected samples were assigned barcodes SPC00503113 through SPC00503124 and sent to the Colloid Laboratory at the Paul Scherrer Institute (PSI) in Switzerland for analysis. All samples were collected in duplicate; upon receipt, one of each type of sample was acidified to a pH of 4. Sample traceability for this water collection is given in Yucca Mountain Project (YMP) Water Binder II, TWS-INC-11-93-08.

### *Colloid generation principles.*

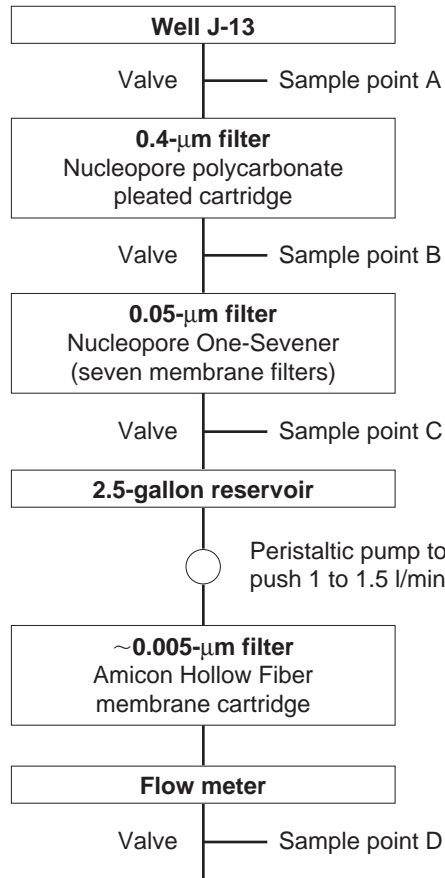
According to the theory of colloid generation, natural colloids are primarily generated by the physical fragmentation and erosion of components of the rock in contact with the water (Degueldre 1994). The colloid size distribution is continuous and may be described by a Pareto power law:

$$\frac{d[coll]}{d\phi} = A \cdot \phi^{-b}, \quad (51)$$

where  $A$  and  $b$  are constants,  $\phi$  is colloid size in terms of the unit size (here 1 nm), and  $[coll]$  is the cumulative colloid concentration for size  $\phi$  in particles/ml. When  $b > 1$ , the cumulative colloid concentration is given as follows for sizes ranging from  $\phi_{\min}$ , the smallest size analyzed, to  $\phi_{\max}$ , the largest size analyzed:

$$[coll] = \frac{A}{1-b} \left( \phi_{\min}^{1-b} - \phi_{\max}^{1-b} \right). \quad (52)$$

Experimentally, an integrated colloid concentra-



**Figure 124. Colloid Sampling.** Flow diagram of the colloid sampling apparatus at Well J-13.

tion, given by Eqn. 52, can be determined over a range from a low value of  $\phi$ , such as the detection limit, to a maximum size, such as 1000 nm, above which colloids are not found in significant concentrations. The integration constant is zero.

By assuming an average colloid density,  $\rho$ , and spherical colloids, determination of the colloid concentration (in terms of mass per unit volume) is possible using

$$\frac{d[\text{coll}]}{d\phi} = \frac{\rho\pi\phi^3}{6} \cdot \frac{d[\text{coll}]}{d\phi}, \quad (53)$$

where  $[\text{coll}]$  may be expressed in  $\mu\text{g/ml}$ .

A surface-complexation capacity may be estimated assuming that the colloids are spherical. Two

hypotheses for site distributions are suggested.

One assumes that surface complexation occurs at the surface of the spherical colloids with an area site density,  $\Delta$ , in sites/ $\text{nm}^2$ ; the second considers the spherical colloids as nanoporous entities with a volume site density,  $\Delta'$ , in sites/ $\text{nm}^3$ . Both minimum and maximum capacities are evaluated using the following equations:

$$\begin{aligned} \left. \frac{\delta[\text{site}]}{\delta\phi} \right|_{\min} &= \pi\phi^2\Delta \frac{d[\text{coll}]}{d\phi} \quad \text{and} \\ \left. \frac{\delta[\text{site}]}{\delta\phi} \right|_{\max} &= \frac{\pi\phi^3}{6} \Delta' \frac{d[\text{coll}]}{d\phi}. \end{aligned} \quad (54)$$

*Analysis of colloid concentrations in J-13 water.*

At the Colloid Laboratory at the PSI, the colloid concentration in J-13 well water was determined by laser particle counting, a technique described previously (Degueldre 1994). After significant dilution in ultrapure water, the natural particles from the groundwater were counted with an argon, 10-mW laser (Horiba PLC311) and analyzed with respect to size according to the intensity of scattered light that the particles produce in the unit laser beam. Information is displayed in a cumulative distribution:

$$[\text{coll}] = \int_{\phi_{\min}}^{\phi_{\max}} \frac{d[\text{coll}]}{d\phi} d\phi, \quad (55)$$

where  $\phi_{\min}$  and  $\phi_{\max}$  are, respectively, the smallest and largest sizes analyzed.

To calculate the colloid concentration (either as particle concentration,  $[\text{coll}]$ , or as mass concentration,  $[\text{coll}]$ ) for a given size range and to calculate normal size distribution (either as  $d[\text{coll}]/d\phi$  or as  $d[\text{coll}]/d\phi$ ), the results from these analyses were treated (by J. C. Loizeau at the University of Geneva) with the PSI code COLIAT (for colloid linear analytical treatment). Two COLIAT options, both based on Eqns. 51 to 53, are available. The first option considers  $A$  and  $b$  as constant over the size range; the second option considers  $A$  and  $b$  as a function of  $\phi$  (although constant in the interval from  $\phi$  to  $\phi + \Delta\phi$ ). Both options assume that all colloids are spherical. Equation 53 relates the



mass and particle concentrations of colloids for a size range on the basis of colloid density. The resulting linear plot is conservative for the small colloids because, in principle,  $b$  decreases when colloid size decreases.

The following observations were made during the analysis of the J-13 well water:

- The concentration of colloids in the acidified samples was the same as the concentration of colloids in the unacidified samples. Thus, removing the water from the subsurface does not seem to cause precipitation of calcium carbonate or other solids that may change the amount of colloids measured in J-13 water.
- The concentration of colloids in samples placed in Teflon containers was smaller than in samples placed in glass containers, probably because of particle adsorption to the walls of the Teflon containers. Thus, a glass container seems to be better than a Teflon container for collecting water samples. A similar result was found during the Grimsel Colloid Exercise (Degueldre et al. 1990).
- The measured colloid concentration in the filtered samples was larger than in the unfiltered samples. Therefore, collecting water from the well itself without further filtration seems to

be the best collection method because filters may add particles to the collected water.

Table 32 summarizes the concentration and characteristics of the colloids in the water from Well J-13 (assuming  $\rho = 2$  g/ml). The Pareto power law (Eqn. 51) yields a value of 3.76 for  $b$  and a value of  $-3.2 \times 10^{12}$  particles/ml for  $A$ . As suggested earlier by Degueldre (1994), when  $b = 4$ , colloids may have been generated by erosion, including, for example, rock multifragmentation. In natural media, however, specific attachment, nucleation, and aggregation may modify the values of  $A$  and  $b$ . In the case discussed earlier, when  $b = 4$ , no aggregation takes place; when  $b < 4$ , aggregation may have occurred.

There is good agreement between the earlier results obtained by Ogard and the results of this study. We found the concentration of colloids larger than  $0.2 \mu\text{m}$  (200–1000 nm) to be  $2.3 \times 10^{-5}$  g/l, which agrees with Ogard's value of  $2.7 \times 10^{-5}$  g/l for the concentration of colloids larger than  $0.4 \mu\text{m}$ .

## Potential Sources of Colloids at Yucca Mountain

Moulin and Ouzounian (1992) pointed out that colloids and organic substances can affect the mobility of radionuclides as a result of complexation, sorption, and dissolution/precipitation. Radioactive waste-derived colloids are degradation col-

**Table 32. Concentration and Characteristics of Colloids in J-13 Well Water**

Particle size (nm)	Number concentration (pt./ml)	Mass concentration (ng/ml)*	Minimum site concentration (nmoles/ml)**	Maximum site concentration (nmoles/ml)**
> 100	$4.2 \times 10^6$	30.6	$1.6 \times 10^{-3}$	$7.6 \times 10^{-2}$
> 200	$3.6 \times 10^5$	23.1	$8.2 \times 10^{-4}$	$5.8 \times 10^{-2}$
> 500	$4.7 \times 10^4$	11.0	$2.4 \times 10^{-4}$	$2.7 \times 10^{-2}$

\*The mass concentration was calculated for a size range of 100 to 1000, 200 to 1000, and 500 to 1000 nm, respectively, using an average colloid density of 2 g/ml.

\*\*Site concentrations were calculated using site densities of 3 sites/nm<sup>2</sup> (minimum) and 3 sites/nm<sup>3</sup> (maximum).

loids, precipitation colloids, and pseudocolloids. Bates et al. (1993) studied the parameters that could affect the reactions of glass waste forms in an unsaturated environment with possible air exchange with adjacent biospheres (typical of what might be expected at Yucca Mountain). Buck et al. (1993) used analytical electron microscopy to study colloid generation from nuclear waste glass reactions. Buck et al. demonstrated that colloids are generated during waste glass dissolution and that the colloids generated often contain radioactive elements.

High-level waste glass in a nuclear waste repository may be contacted by water vapor, small amounts of sorbed liquid water, or flowing water (Bates et al. 1992). Bates et al. used a test method that involved dripping water onto a glass-metal assembly suspended in a vessel. Water collected in the bottom of the vessel was filtered to determine whether the actinides neptunium, plutonium, and americium were associated with particulates or dissolved in solution. They reported that 70 per cent of the neptunium passes through 1-nm filters and can be considered truly dissolved. Over 99 per cent of the plutonium and americium in the test groundwater is concentrated in colloidal particles that are fragments of a hydrated layer that spalls from the glass surface during aqueous alteration.

Feng et al. (1993) studied the colloids generated from the interaction of high-level nuclear waste glasses with groundwater at 90°C. The tests consisted of immersing powder glass in water from Well J-13. The Teflon™ test vessel was then tightly sealed and placed in a 90°C oven. After termination of a test, settling was allowed to occur at room temperature overnight. The resulting glass leachate was analyzed for colloids. Feng et al. concluded that waste glass contributes to the formation of colloids by 1) increasing ionic strength of the groundwater (which leads to nucleation), 2) releasing radionuclides that form pseudocolloids (by sorbing to groundwater colloids), and 3) spalling fragments of colloidal size from the surface layer of the reacted glass. They report that 1)

the colloids found in the leachate are mainly silicon-rich smectites and uranium silicates; 2) colloids in the leachate agglomerate when the salt concentration is high but the agglomerated colloids can resuspend if dilution takes place; 3) colloids in the leachate agglomerate quickly after the leachate is cooled to room temperature, and most of the colloids settle out of the suspension after the leachate has been at ambient temperature for a few days; and 4) the colloids in the leachate are negatively charged between pH values of 1 and 10.5. Feng et al. inferred from these studies that 1) in a glass-reaction-dominated repository environment, where salt concentrations are likely to be high, the colloid concentration is likely to be low and the colloid transport of radionuclides will be minimal; 2) if a large amount of groundwater contacts the glass reaction site, the colloids that have settled out of suspension may resuspend and colloid transport may be important; and 3) at ambient temperatures, the colloids may agglomerate quickly and settle out of suspension in a short time.

Real Pu(IV) colloids, produced by the agglomeration of hydrolyzed Pu(IV) ions under acidic conditions have been reported by Hobart et al. (1989) and Triay et al. (1991a). Hobart et al. provided evidence that colloidal Pu(IV) is electrochemically reactive and structurally similar to plutonium oxide. Triay et al. reported stable Pu(IV) colloids under acidic conditions in the size range from ~1 nm to 0.4 mm. These Pu(IV) real colloids, generally referred to as Pu(IV) polymers, may not be stable at near-neutral pH values. In addition, the actinide colloids have a positive surface charge and would be expected to attach to tuffs at Yucca Mountain with negative surface charges. However, the formation of actinide pseudocolloids in groundwaters has been reported in numerous studies and reviewed by Kim (1991).

The existence and formation mechanisms of natural colloids at Yucca Mountain that may allow the generation of pseudocolloids at the potential repository have been studied by Levy (1992). Materials of potential interest include both gels that are still

liquid-rich and former gels that have solidified and crystallized. The materials studied by Levy include cores and sidewall samples from drill holes at Yucca Mountain and semi-transparent fluid-gel samples from tunnel exposures at Rainier Mesa. Both Yucca Mountain and Rainier Mesa (40 km from Yucca Mountain) consist of ash-flow and bedded tuffs. Levy reports that diagenetic and hydro-thermal alteration of volcanic glass are responsible for the genesis and deposition of gels at Yucca Mountain. The principal gel products at Yucca Mountain and Rainier Mesa were heulandite-clinoptilolite, silica minerals, and smectite. Given the heat generated by the potential repository (Buscheck and Nitao 1993) in devitrified Topopah Springs tuff, recharge water, or reflux water concentrated by the repository, Levy predicts that thermal effects may be sufficient to cause local alteration of glass in the underlying vitrophyre and colloid formation.

Kim (1991) pointed out the potential importance of microorganisms as colloids that can bind radionuclides and migrate through the subsurface. Bales et al. (1989) described the use of bacteriophage to study transport through sandy soil and fractured tuff. Bales et al. report that 1) virus particles can travel several meters in sandy aquifers, 2) the apparent exclusion from 35 to 40 per cent of the pore volume in a granular medium suggests that virus will travel 1.6 to 1.9 times faster than a conservative tracer, and 3) results from granular-medium and fractured-tuff experiments illustrate the inability of a soluble conservative tracer to provide estimates for the dispersion and effective porosity applicable to a colloid.

Choppin (1988) pointed out the importance of humic materials on metal-ion speciation and behavior in geologic systems at concentrations as low as 0.1 ppm. Minai et al. (1992) measured the binding constant of the humic- and fulvic-acid fractions in water from Well J-13 for Am(III); they report that these binding constants are similar to those of other aquatic materials. Based on a concentration in J-13 water of 0.01 to 0.1 ppm for total

organic content, Minai et al. conclude that the americium-humate complex could be a significant species in J-13 water. Although Minai et al. did not measure any other actinide with the humic material from J-13 water, they extrapolated from other studies. Uranyl speciation would not be affected in J-13 water unless the total organic content is greater than 0.2 ppm. Minai et al. indicate that humic material at ppm levels reduces Pu(VI) and Pu(V) to Pu(IV); consequently, plutonium present in the V and VI oxidation states would be reduced to the IV state. If the Eh is low enough to allow formation of Pu(III), then plutonium speciation would be affected by humics in the same manner as Am(III).

## Laboratory Experiments on Colloid Stability

To ascertain the conditions under which colloids would remain in suspension, we performed a series of laboratory aggregation experiments to determine the stability of colloids in synthetic and natural groundwaters as a function of groundwater chemistry. We used the results of our experiments to calculate particle-aggregation rate constants and to establish the stability of colloids. From the standpoint of colloid-facilitated transport to the accessible environment, only stable suspensions, suspensions that exhibit reversible aggregation, and suspensions that exhibit exponential aggregate growth at a comparable time scale as advective transport are of concern. Consequently, the stability of a particulate suspension is a question of the kinetics of aggregation as well as of the structure of the resulting aggregate.

For the stability investigations, we chose particles of kaolinite clay and amorphous silica because of their prevalence in the natural environment, their previous use in aggregation studies, and the requirement that particulate suspensions be made in a consistent and reproducible manner. Silica particles from the Nissan Chemical Co. were cleaned by repeated centrifugation, decanting, and resuspension in ultrafiltered deionized water until the conductivity of the particulate suspension was

40  $\mu\text{S}/\text{cm}$  or less for three consecutive washings. Kaolinite clay was acid washed and repeatedly cleaned (van Olphen 1977). The hydrodynamic mean diameter and particle-number concentration were 85 nm and  $1.75 \times 10^9$  particles/ml, respectively, for the silica particles and was 200 nm and  $1.59 \times 10^9$  particles/ml, respectively, for the kaolinite clay particles.

The chemical composition of the aqueous medium was designed to mimic groundwater compositions at Yucca Mountain (Kerrisk 1987). We prepared particle stock solutions by resuspending the sols in a carbonate-rich solution ( $0.368 \text{ mM Na}_2\text{CO}_3 + 10.600 \text{ mM NaHCO}_3$ ) having a pH of 7.8. All experiments were performed at  $27.5^\circ\text{C}$ . We induced aggregation by adding sufficient NaCl electrolyte solution to the prepared particulate suspensions to achieve a final NaCl concentration ranging from 100 to 800 mM. We ascribe observed differences in particle-aggregation rates to differences in solution chemistry (ionic strength) and particle composition.

We used autocorrelation photon spectroscopy (APS) to estimate the particle-aggregation rate constant for the early stages of the aggregation process. APS is sensitive to fluctuations in scattered intensity resulting from the Brownian motion of particles. The fluctuations in scattering intensity yield an intensity autocorrelation function in which the mean decay constant can be directly related to a mean diffusion coefficient (Ostrowsky 1988; Brown and Pusey 1975; and Amal et al. 1990). Particle size is related to the mean diffusion coefficient,  $D_{\text{mean}}$ , by the Stokes-Einstein relation:

$$D_{\text{mean}} = \frac{k_B T}{3\pi\eta\phi_{\text{mean}}} , \quad (56)$$

where  $k_B$  is Boltzmann's constant,  $T$  is the temperature in degrees Kelvin,  $\eta$  is the viscosity of the suspending liquid, and  $\phi_{\text{mean}}$  is the hydrodynamic mean diameter of the particles. Because aggregate growth changes the particle size distribution over time, the rate of aggregation can be estimated using Eqn. 56 by determining the rate of decrease in the

mean diffusion coefficient. The interpretation of diffusion coefficients, and consequently  $\phi_{\text{mean}}$ , measured by APS is affected by polydispersivity, particle shape, and particle-particle interactions. In this study, we handled the effect of polydispersivity and particle shape on the autocorrelation function satisfactorily by preparing essentially monodispersed particle solutions, which allowed us to discard the higher-order terms of the cumulant method.

For a discrete particle size distribution, the generation of doublets by collisions of primary particles is represented by a second-order rate law (Stumm and Morgan 1981):

$$\frac{\partial[\text{coll}_I]}{\partial t} = -k_{II}[\text{coll}_I]^2 , \quad (57)$$

where  $k_{II}$  is the rate constant for doublet formation and  $[\text{coll}_I]$  is the number concentration of primary particles. Aggregation rate constants,  $k_{II}$ , were calculated from the initial slope of a plot of  $\phi_{\text{mean}}$  as a function of time,  $t$ , using

$$\phi_{\text{mean}} \cdot k_{II} = \frac{1}{F \cdot [\text{coll}_I]_{t=0}} \cdot \frac{\partial\phi_{\text{mean}}}{\partial t} , \quad (58)$$

where  $F$  is an optical factor and  $[\text{coll}_I]_{t=0}$  is the initial number concentration of primary particles (Virden and Berg 1992). Because partial aggregation of the initial dispersion affects the analysis of the aggregation kinetics, we implemented a correction procedure to account for the initial size distribution of the aggregates. The correction was accomplished by projecting the slope of a plot of the function  $\phi_{\text{mean}}$  to a time point where  $\phi_{\text{mean}}$  corresponds to the initial (monodispersed) suspension.

APS measurements were made with a laser light-scattering system (Brookhaven Instruments) equipped with an argon laser (Innova 90) operating at  $\lambda = 514 \text{ nm}$  and 0.5 to 1.0 W. Sampling times are dependent on particle concentration and ionic strength of the medium. Experimental run times for the aggregation experiments were typically 60 minutes (longer run times are necessary for highly stable colloids). Measurements of the hydrodynamic diameter,  $\phi_{\text{mean}}$ , were made every minute

using a sampling duration of 30 seconds. All measurements were made at a scattering angle of  $90^\circ$ .

The experimental results (Figs 125 and 126) characterize the aggregation process of silica and kaolinite clay. Aggregation of silica particles and kaolinite clay particles decreased dramatically for an electrolyte concentration,  $C_{\text{NaCl}}$ , below 300 mM and 200 mM, respectively.

However, it is possible that reversible aggregation occurs in this concentration range if a secondary minimum, distinguished by the absence of a potential barrier in the potential curve, is present (Overbeek 1952). However, the duration of the current set of experiments was too short to resolve aggregate growth at this level of detail (Cametti et al. 1989). When the concentration of electrolyte is increased to induce aggregation, aggregate growth proceeds at an exponential rate, is irreversible, and the rate of aggregation increases with increasing electrolyte strength. The relationship between electrolyte strength and growth rate is evident for kaolinite clay particles at  $C_{\text{NaCl}}$  between 100 and 300 mM (as shown in Fig. 126). At high electrolyte concentrations, the rate of aggregation slows down abruptly after the initial rapid growth phase. The first stage of exponential growth is characterized by reaction-limited aggregation (RLA), and the second stage of the growth curve is characterized by diffusion-limited aggregation (DLA). The rapid and slow regimes of aggregation have been observed in various particulate systems, such as polystyrene, gold, and silica colloids (Cametti et al. 1989).

Aggregation rates are readily expressed in terms of stability,  $W$ , defined as the ratio between the Smoluchowski rate constant,  $k_{\text{smol}}$ , and the experimentally attained rate constant:

$$W = \frac{k_{\text{smol}}}{k_{\text{II}}} , \quad (59)$$

where  $W$  is a dimensionless parameter and  $k_{\text{smol}}$  is obtained from the Smoluchowski equation for doublet formation:

$$k_{\text{smol}} = \frac{8k_{\text{B}}T}{3\mu} , \quad (60)$$

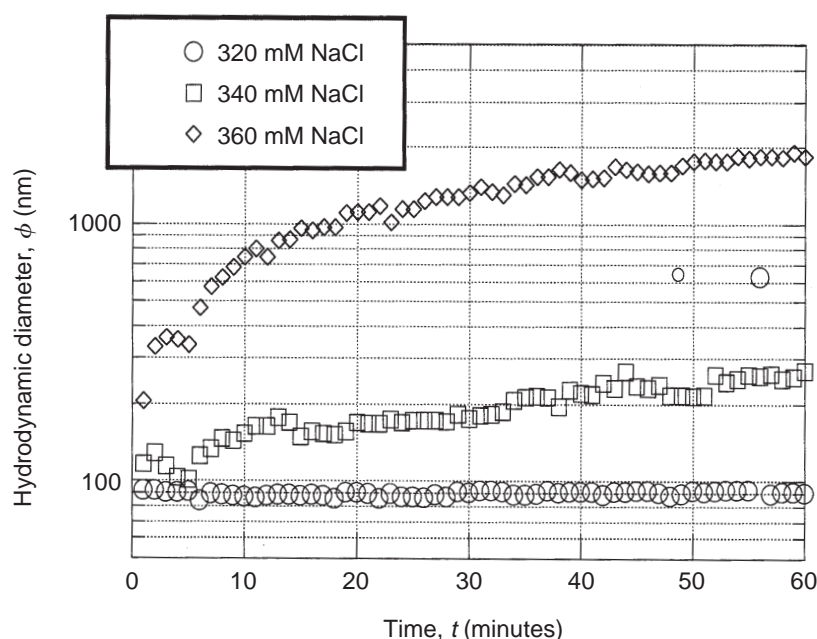
where  $T$  is absolute temperature and  $\mu$  is the dynamic suspension viscosity (Stumm and Morgan 1981). The effect of varying electrolyte concentration is shown in Fig. 127.

Kaolinite clay particles are destabilized at a lower electrolyte concentration than are silica particles. Also evident is the gradual increase in stability of the clay particles, compared with the abrupt transition from unstable to stable behavior exhibited by the silica particles. Kaolinite clay is characterized by the negative surface charge on the clay face, which is a result of isomorphic substitution and the electronegative character of the oxygen atoms, and by a positive charge on the mineral edges, which is a result of exposed cations. Thus, when the clay minerals are suspended in waters with low electrolyte concentration, collisions may produce aggregates having an open and porous structure. At higher electrolyte concentrations, the repulsive forces may be suppressed to allow aggregation into denser structures.

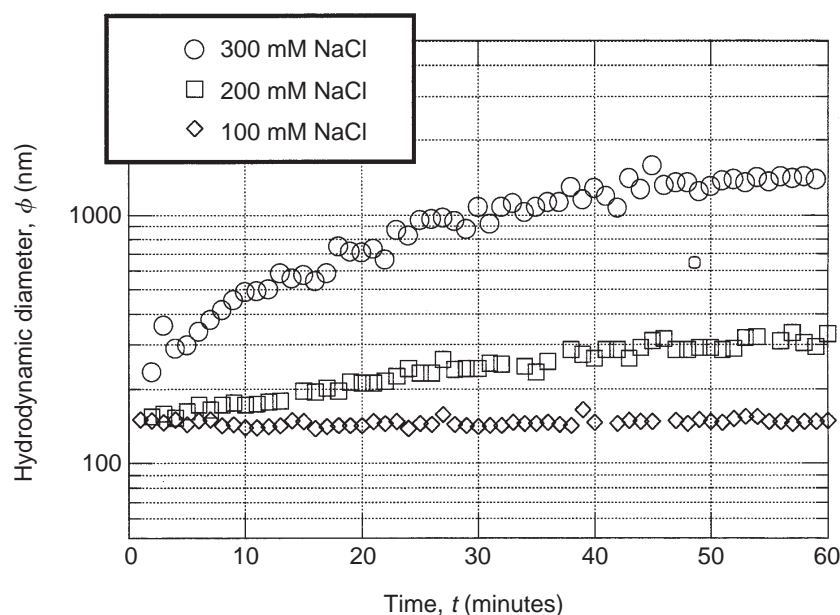
For slow aggregation processes, the time scale for aggregate rearrangement and consolidation is long compared with the time scale of collision, whereas for rapid or irreversible aggregation, rearrangement is less probable. If consolidation does take place, then aggregates having a uniform surface-charge distribution could form more compact and dense clusters during slow aggregation and more open clusters under fast aggregation. Consequently, colloid stability is a function of particle charge, surface-charge distribution, and aggregation kinetics (Lips and Duckworth 1988). The experimentally determined particle-aggregation constants may be used in transport models to assess the mobility of subsurface colloids along given flowpaths as a function of groundwater chemistry.

Thompson (1989) studied the retardation of Pu(IV) real colloid (polymer) and Am(III) through columns made of crushed tuff from Yucca Mountain (in the grain size range from 75 to 500  $\mu\text{m}$ ).





**Figure 125. Aggregate Growth for Silica Particles.** Here,  $\phi_{\text{mean}} = 85 \text{ nm}$  at  $t = 0$ , and the pH is 7.8. The flatness of the bottom curve ( $C_{\text{NaCl}} = 320 \text{ mM}$ ) indicates a steady-state condition with no aggregation; the middle curve ( $C_{\text{NaCl}} = 340 \text{ mM}$ ) shows reaction-limited aggregation (RLA); and the upper curve ( $C_{\text{NaCl}} = 360 \text{ mM}$ ) shows reaction-limited aggregation initially and diffusion-limited aggregation (DLA) later.



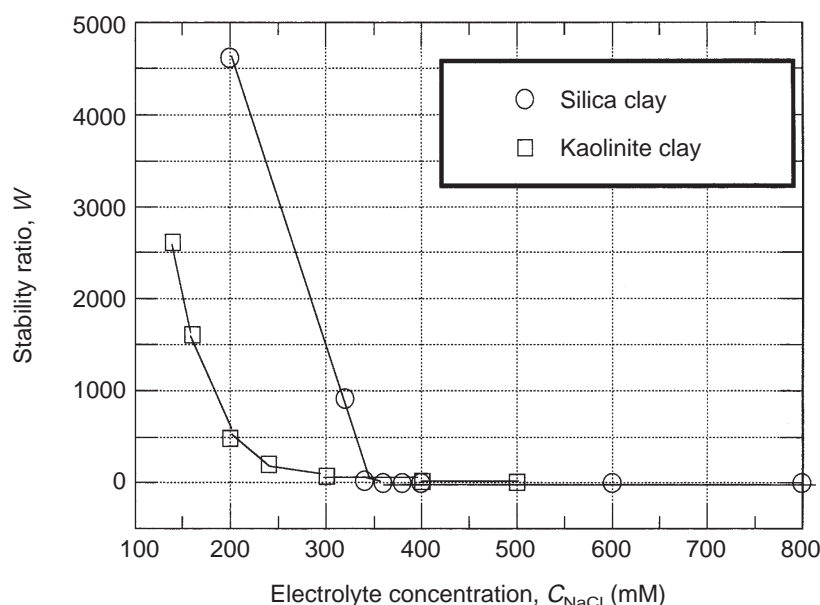
**Figure 126. Aggregate Growth for Kaolinite Clay Particles.** Here,  $\phi_{\text{mean}} \sim 200 \text{ nm}$  at  $t = 0$ , and the pH is 7.8. The lowest curve ( $C_{\text{NaCl}} = 100 \text{ mM}$ ) suggests a steady-state condition with no aggregation; the middle curve ( $C_{\text{NaCl}} = 200 \text{ mM}$ ) shows reaction-limited aggregation (RLA); and the upper curve ( $C_{\text{NaCl}} = 300 \text{ mM}$ ) shows reaction-limited aggregation initially and diffusion-limited aggregation (DLA) later.

The columns used for the study were 5 cm long and 0.45 cm in diameter with a porosity of 0.5 to 0.6. The interstitial velocity used for these studies was 150 m/yr. The Pu(IV) real colloid used by Thompson for these experiments ranged in size from 50 nm to 0.4 mm. Thompson reports that Pu(IV) real colloid and Am(III) are largely retained by the tuff, with a small fraction of the injected material moving through the columns faster than the tritiated water (used as the conservative tracer).

Rundberg et al. (1989) measured the migration of colloidal polystyrene tracers through a saturated fractured-tuff column. The fractured-tuff sample was an outcropping from Fran Ridge (near Yucca Mountain). The fractures in this sample were originally filled with calcite; after the fractured-tuff sample was encapsulated for tracer elution, the calcite was leached with dilute hydrochloric acid. Transport in this fracture sample was not describ-

able using the cubic-law aperture determined from the fracture permeability. To fit the elution data for a conservative tracer, adjustment of the fracture aperture was required. Rundberg et al. report that polystyrene colloids with a  $\sim 1$ -mm diameter were found to have the lowest filtration coefficient, which is in qualitative agreement with the filtration model considered by Rundberg et al.

The relevance of these column studies for the prediction of colloid-facilitated radionuclide transport at Yucca Mountain is difficult to assess. Thompson's experiments were conducted with crushed tuff. The work of Rundberg et al. was conducted both by using fractures that were severely altered by the addition of dilute hydrochloric acid to dissolve the calcite fillings and by using colloids (such as polystyrene spheres) that are not representative of those at Yucca Mountain. The small scale of both sets of column experiments is



**Figure 127. Stability Curves.** The stability ratio,  $W$ , is shown for silica and kaolinite clay particles in synthetic groundwater at a pH of 7.8 as a function of sodium chloride electrolyte concentration,  $C_{NaCl}$ . The  $k_{smol}$  factor in the stability ratio ( $W = k_{smol}/k_{II}$ ) remains constant with changing electrolyte concentration, but  $k_{II}$ , the kinetic rate factor for doublet formation, varies and, in fact, approaches  $k_{smol}$  in value as the electrolyte concentration increases. As a result,  $W$  approaches a minimum value of 1 at high electrolyte concentrations.

not comparable to the large scales available for colloid filtration at Yucca Mountain.

## **Future Direction of Colloid Studies in the Yucca Mountain Site Characterization Project**

Degueldre (1993) presented a strategy to study the importance of colloid-facilitated radionuclide transport in granitic systems. This strategy was carefully considered in the development of the colloid strategy to assess the importance of colloid-facilitated radionuclide transport at Yucca Mountain. The strategy consists of asking the following:

- 1) Will radioactive waste-derived colloids be present at the potential repository?
- 2) Will these colloids be stable in the likely groundwaters?
- 3) Can these colloids migrate over field-scale distances?

### **Will radioactive waste-derived colloids be present at the potential repository?**

In regard to first question, laboratory experiments similar to the ones being performed by Bates et al. (1992, 1993) will address the generation of degradation colloids from high-level waste glass forms. This type of study will provide a degradation-colloid concentration source term for the performance assessment calculations for the potential repository that will include the actinide content of the degradation colloids.

The formation of colloids by natural glass alteration in a repository hydrothermal environment will be addressed by natural analog studies at Yucca Mountain. The natural hydrothermal alteration that occurred in the cooling pyroclastic deposits 12 to 13 million years ago may be a useful analog to a waste repository environment. Relict colloidal material has been identified among the alteration products in the glassy rocks below the potential repository.

The surface charge of radiocolloids (such as plutonium colloids) is positive; consequently, radiocolloids will attach to Yucca Mountain tuff, which has a negative surface charge at near-neutral pH values, and become immobilized. However, the formation of pseudocolloids from the sorption of real actinide colloids onto groundwater colloids is of concern. The generation and properties of real actinide colloids will be studied using the methods presented by Hobart et al. (1989) and Triay et al. (1991a).

Understanding the formation of pseudocolloids requires knowledge of the groundwater colloids at Yucca Mountain. To address the generation of groundwater colloids at Yucca Mountain, we will collect samples at selected sites in the vicinity of the potential repository block in an attempt to quantify and qualify the presence of inorganic colloids, high- and low-molecular-weight dissolved organic carbon compounds, and selected microorganisms in saturated-zone ground waters. Limitations on uses of the data derived from the samples will be a function of the extent to which samples represent the medium from which they are extracted. This point raises fundamental concerns about sample representativity and integrity.

We will collect samples from discrete intervals isolated by pneumatic packers, generally in uncased boreholes. Interval lengths likely will range between 2 and 20 m and will be selected based on borehole televiwer and caliper data. Borehole wall rugosity and fracture distribution and orientation will be primary factors used to determine packer locations. Rates of withdrawal from different intervals will range from about 0.5 to 2.0 l/min and will be selected to minimize horizontal shear velocities at the borehole wall in order to preclude or minimize detachment and entrainment of non-suspended particles. Preliminary determination of velocity constraints will begin with information reported by Hunt (1982), Hubbe (1985a, 1985b), and Ryan (1988). We will construct the pump and isolation equipment within the borehole (packers, screens, and adjacent tubing) from stainless steel,

and the tubing used to transport samples up-hole to the mobile laboratory at the well head will be either nylon, polypropylene, or Teflon™. Our preparation will include efforts to preclude, minimize, or identify sampling-system effects on microbiologic samples.

Sample integrity will be influenced by the means used to collect and store raw samples and by the means used to isolate or concentrate colloidal phases. For example, microbiologic samples will be collected using aseptic procedures. The perceived options include centrifugation, filtration, and sedimentation, and it is assumed that pumping and isolation equipment do not deleteriously influence sample quality.

However, knowing that filtration methods can induce data artifacts (Rees 1990, p. 2777), we can use isolated-sequential filtration similar to that carried out by Ogard (1987) to preclude atmospheric influences and enable maintenance of sufficient pressure to satisfactorily prevent carbon-dioxide degassing with its attendant pH change. This method also is conducive to accumulating relative large masses of particles.

Tangential-flow filtration is a closed-system method that also can be used to process large volumes and yield particle concentration increases of at least two orders of magnitude. It is conceivable, however, that the recirculating tangential technique can disaggregate natural particles. An alternative to isolated sampling is an adaptation of the method developed by Degueldre and Thomi (1986) for pulsed diaultrafiltration under a controlled mixed-gas atmosphere, the carbon-dioxide partial pressure of which is determined using any of several geochemical codes.

We will measure particle properties quantitatively or qualitatively, as deemed appropriate, using one technique or a combination of several techniques. If feasible, either absolute inorganic colloid concentrations or size-range concentrations will be determined on site at selected intervals during

pumping to provide transient information relative to representativity and to final representative concentration data. If this is not possible, periodic samples will be collected during pumping for subsequent separation and analysis. Particles as small as 1 nm can be filtered from discrete aliquots, counted, and size distributions measured using scanning (Degueldre et al. 1989a, 1989b) or transmission electron microscopy (Gschwend and Reynolds 1987; Ryan and Gschwend 1990) and attendant energy-dispersive spectroscopy or atomic-force microscopy (Emch et al. 1992; Zenhausern et al. 1992). Phases can also be identified by determination of bulk chemistry of filtered material and perhaps by x-ray diffraction analysis of particles of sufficient size.

We will measure, quantitatively and qualitatively, dissolved organic carbon contents of groundwaters, and the attendant high- and low-molecular-weight carbon fractions, represented generally as humic and fulvic acids.

We will study the sorption behavior of the actinides (plutonium, americium, uranium, and neptunium) onto the groundwater colloids to form pseudocolloids (Vilks and Degueldre 1991) in order to determine radionuclide distributions between the colloids and the groundwaters and to assess the reversibility of the sorption mechanism of radionuclides onto colloids. Spectroscopy studies will provide supplemental information by identifying the mechanisms of radionuclide sorption onto colloids. We will also study the formation of humic or fulvic pseudocolloids with the actinides in the organic fractions isolated from the saturated-zone colloidal fraction in order to assess the importance of actinide-humate or fulvate species. These various studies will yield groundwater colloid concentrations and the capacity of the colloids to carry radionuclides.

## **Will radioactive waste-derived colloids be stable in the likely groundwaters?**

In regard to this second question, given the thermal loads being considered for the potential repository,

elevated temperatures are expected in the near field (Buscheck and Nitao 1993); consequently, colloids in the near field will not be stable. We will study the stability of degradation colloids as a function of temperature and likely water chemistries in the unsaturated zone using the colloids generated in the laboratory experiments to address colloid formation at the potential repository (Bates et al. 1992, 1993). We will study the stability of radio-colloids, groundwater colloids (silica, zeolites, and clays), and pseudocolloids as a function of unsaturated- and saturated-zone water chemistry and temperature. The studies will incorporate a range of calcium concentrations representative of the Yucca Mountain vicinity. Degueldre (1993) was able to correlate the concentrations of colloids in different granitic systems with the calcium concentration of the groundwater at those sites. Even though Kingston and Whitbeck (1991) did not find any correlation of the colloid concentrations at the Nevada Test Site with the groundwater chemistry, it is possible that the correlation exists and that the data of Kingston and Whitbeck is the result of particulate contamination during sampling.

## **Can radioactive waste-derived colloids migrate over field-scale distances without being removed by filtration?**

We will address the mobility of the colloids through the medium at Yucca Mountain by conducting transport experiments. Laboratory-scale column experiments that involve the elution of well-characterized colloids (such as polystyrene spheres), degradation colloids, radiocolloids, and pseudocolloids through porous and fractured-tuff columns will be used to validate a transport code capable of describing colloid transport (such as the FEHM or CTCN codes). These studies will yield attachment/detachment parameters for colloids migrating through tuff that can be used in performance assessment calculations.

We will perform experiments in which colloids are eluted through a large lysimeter filled with porous media and blocks ( $\sim 1 \text{ m}^3$ ) of fractured tuff. Such experiments will address the gap between laborato-

ry and field scales.

We will study field-scale colloid transport in unsaturated, fractured tuff (Hunt 1993). Hunt's proposal for such a study involves weapons tests at the Nevada Test Site, which could provide a worst-case scenario by evaluating whether or not radionuclides have leached beneath a weapons test that was fired above the water table. Hunt points out that a nuclear weapons test is similar to a high-level nuclear waste repository. A weapons test emplaces long-lived radionuclides within a fractured formation and within molten glass. The heat gradually diffuses away, and water enters the test cavity (first as a vapor and then as a condensed liquid partially coating the surfaces). This water would promote glass and mineral weathering. The weapons test can also produce a surface crater that will act as a collection point for precipitation and accelerate infiltration. Hunt proposes the use of a test site in which 1) the weapons cavity is at least 100 m above the water table (so that enough unsaturated-zone space exists beneath the cavity to carry out an adequate study), 2) the nuclear weapons test has produced a surface depression that would accelerate and concentrate water infiltration, and 3) the test should have occurred at least 10 years ago to allow for heat dissipation and water infiltration. Sampling the rock around and beneath this test would provide data that represents a worst-case scenario for Yucca Mountain—that is, an unpackaged waste-containing glass subjected to water and infiltration through partially saturated freshly-fractured tuff.

We will study field-scale colloid transport in the saturated zone by injecting polystyrene microspheres during cross-hole hydraulic testing at a well complex at Yucca Mountain (C-Wells). This effort will provide an opportunity to study colloid transport through saturated, fractured tuff and will simulate a scenario involving formation of pseudocolloids that reach the groundwater table at Yucca Mountain. The idea of the C-Wells field experiments is to inject various tracers (including well-characterized colloids) into the saturated zone via



an injection well and then observe the appearance of these tracers in sampling wells at downgradient locations.

The field experiments will allow the validation of a transport code to predict colloid transport through fractured tuff at large scales. If validation results are satisfactory, this code can then be used to perform sensitivity analyses that would identify the information that needs to be considered in a performance assessment to address the importance of colloid-facilitated radionuclide transport from the potential repository at Yucca Mountain.

In summary, the currently available information on colloid transport is not sufficient to conclude that colloids will not be able to carry radionuclides from a repository to the accessible environment at Yucca Mountain. In order for colloids to facilitate radionuclide transport at Yucca Mountain, they must be present in stable suspensions in sufficient quantities, the radionuclides must be associated with the colloids, and the colloids must be transported over field-scale distances. Consequently, the strategy developed above addresses these three main issues, which are critical to assessing the importance of colloid-facilitated radionuclide transport at a nuclear waste repository.

## Conclusions and Summary of Data Needs for Colloid Investigations

A sensitivity analysis study to assess important parameters for colloid-facilitated radionuclide transport can be performed. The following assumptions could be made for this calculation.

- 1) The colloids generated are clays, silica, and iron oxides.
  - 2) The amount of total organic carbon (TOC) in groundwaters is negligible.
  - 3) The stability ratio of the colloids can be estimated on the basis of the data observed for model colloids.
  - 4) The sorption of radionuclides onto colloids ( $K_p$ ) can be calculated on the basis of available values of sorption distribution coefficients ( $K_d$ ) (or on the basis of  $K_p$  values from the literature:  $\sim 3 \times 10^4$  ml/g for the trivalent and tetravalent actinide species).
  - 5) Irreversible sorption of radionuclides onto colloids occurs.
  - 6) No attachment of colloids onto fracture walls occurs.
  - 7) Colloids are excluded from tuff pores by their size and charge.
- Depending on what parameters are the most important in controlling colloid-facilitated radionuclide transport, the following data needs may exist:
- experimental determination of type of colloids generated from spent fuel (to address assumption 1);
  - study of Yucca Mountain as its own analog (to address assumption 1);
  - experimental determination of total organic carbon (TOC) in groundwaters on-line (to address assumption 2);
  - experimental determination of colloid population and size distributions in groundwaters using off-line particle-counting techniques (to address assumptions 3 and 5), because  $K_p$  depends on particle size);
  - experimental determination of selected  $K_p$  values for clay and silica using likely groundwaters (to address assumption 5);
  - experimental determination of the degree of colloid attachment to fracture walls using fractured-tuff columns (to address assumption 6);
  - transport field experiment (under saturated

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conditions) in the C Wells (to address assumption 7); and

- transport field experiment (under unsaturated conditions) using nuclear test at the Nevada Test Site as a source term (to address assumption 7).

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